Photoelectron Spectroscopy of Plutonium at the Advanced Light Source

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We are developing a program to perform Photoelectron Spectroscopy and X-Ray Absorption Spectroscopy upon highly radioactive samples, particularly Plutonium, at the Advanced Light Source in Berkeley, CA, USA. First results from alpha and delta Plutonium are reported as well as plans for a dedicated spectrometer for actinide studies.

I. Introduction

Photoelectron Spectroscopy and X-Ray Absorption are being used to investigate the electronic structure of alpha and delta Pu. [It is generally believed that alpha is more free electron like and delta is possibly a correlated electronic system, although this has yet to be unequivocably proven and the details of which remain clouded.] Our preliminary results[1], where Resonant Photoemission was used to probe large grain polycrystalline delta and polycrystalline alpha, have lead us to modify our initial plans. For example, during the last year we have embarked upon a building project, developing a dedicated Pu Spectrometer at the Advanced Light Source. One result of our first studies is that we believe that minimization of sample oxidation is a key to successful experimentation and we are pursuing that vigorously. Additionally, it now appears that a new experiment, based upon "Double Polarization," may be the key to differentiating between the several models now being proposed to explain the electronic structures of alpha and delta Pu. Here the combination of a chiral xray environment and true spin detection will allow us to test whether spin-orbit, exchange, coulombic repulsion or other multielectronic effects drive the differences between alpha and delta Pu.

II. Experimental

The first experiments were performed at the Spectromicroscopy Facility (Beamline 7.0) at the Advanced Light Source in Berkeley, CA [2]. The Pu samples were taken from a specially purified batch of Pu metal. The plutonium was zone refined and vacuum distilled while magnetically levitated[3] . The product of the purification process was α-Pu containing a total of 170 ppm impurities. A portion of the refined metal was alloyed with gallium to form the δ-phase (fcc symmetry). The sample surfaces were prepared by repeated room-temperature, sputter-annealing cycles to minimize the amount of oxygen and other impurities dissolved in the sample or at grain boundaries, in a specially designed chamber attached to the sample introduction and analysis systems on Beamline 7.0. The transfer, preparation, and analysis chambers ensured that the Pu metal samples did not experience pressures greater than 10^{-8} torr. This minimized any surface contaminants that could adversely effect the soft x-ray measurements.

III. Discussion

Using the tunabilty of synchrotron radiation, it is possible to perform many variants of photoelectron spectroscopy and x-ray absorption, including accessing the core levels of the sample constituents. One of the variants that was pursued was Resonant Photoemission. [4] Photoelectron spectroscopy is a "photon in, electron out" process. Often, it can be simplified down to a single electron phenomenon, where the energy of the photon is absorbed and transferred over entirely to a single electron, while all other "spectator" electrons essentially remain frozen. An advantage of this is its simplicity of interpretation. But in many systems, it is possible to induce a process with heightened sensitivity and significantly increased cross sections: resonant photoemission (ResPes)[4-8] . Here, a second set of indirect channels open up, which contribute in concert with the original or direct channel of simple photoemission. Shown in Figure 1 is a schematic illustrating the resonant photoemission process in Pu, involving the 5f and 5d electrons.

The Pu5f5f5d resonant photoemission process occurs over the photon energy range of 90eV to 150eV, with an antiresonance near 100eV and a resonace maximum near 120eV. (See Figure 2.) In our experiments, both alpha and delta Pu samples have been investigated. The valence band ResPes Spectra (Figure 3) exhibit only small differences between the alpha and delta phase samples. These observations correlate well with the recent results of Gouder et al[9], Arko et al[10] and earlier work of L.E. Cox[11], which suggest that surface reconstruction may be an important issue in Pu samples. Nevertheless, subtle yet possibly significant differences can be observed between the α and single crystallite δ samples, particularly at the Fermi energy and near a photon energy of 130eV. These results suggest that the valence electronic structure of Pu is dependent upon its phase and chemical state. Overall the two sets of spectra strongly resemble each other and confirm the observation of Pu 5f ResPes.

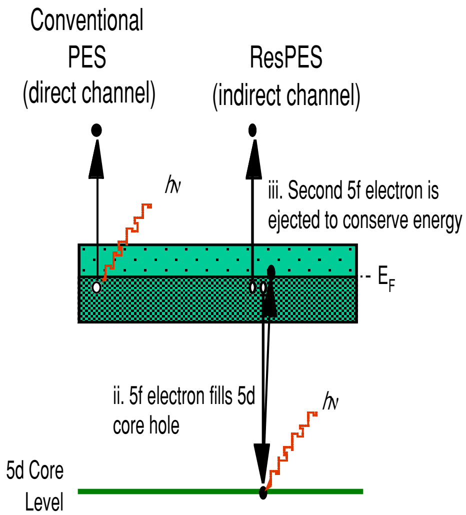

Figure 1. The Resonant Photoemission (ResPes) process for the Pu 5f and 5d states is shown here.

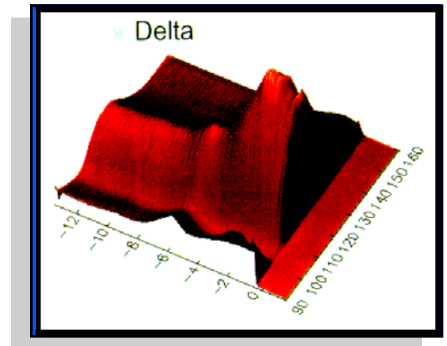

Figure 2. Resonant Photoemission or ResPes is a type of spectroscopic interrogation of the valence electronic structure. A large data set is shown here, for single crystallite delta. The plots show the intensity variations (z axis) versus the binding energy of the states (the negative numbers in eV; zero is the Fermi energy) and photon energy(between 90eV and 160eV).

The similarity of the alpha and delta samples raises an unsettling question. Are the phase actually what we think they are? A means to address this issue and related surface quality questions is to investigate the core level spectroscopy of the Pu and possible additional elemental constituents. Some our results are shown in Figure 4 below.

The spectra in Figure 4a confirm that we have phase specific samples. The alpha and delta are each consistent with earlier reported results[12-15]. Furthermore, the wide scan (Fig 4b) and details of the O1s (Fig 4c) and C1s (Fig 4d) regions at 1250eV confirm that our samples are quite "clean." However, the spectra at 850eV illustrate an interesting point: by tuning to energies where the O1s and C1s cross sections are larger, there is a significant improvement in sensitivity to oxygen and carbon surface degradation. In the future, this will permit us to study surface oxide and carbide formation with improved and lower detection limits.

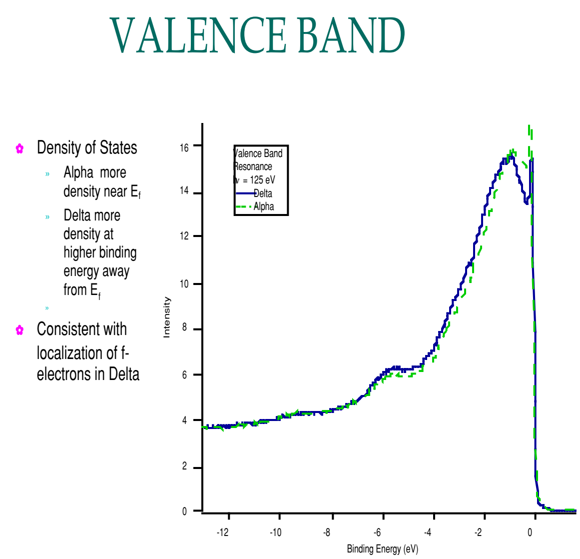

Figure 3. Comparison of the valence band spectra of alpha and delta Pu at a photon energy of 125eV.

Finally, we are presently constructing a new dedicated Pu Spectrometer, a schematic of which is shown in Figure 5. This spectrometer will include specialized capabilities for handling Pu samples. For example, the long vertical manipulator will allow the isolation of the radioactive byproducts of sample preparation and cleaning from the analysis station yet also permit rapid access of the analysis position, so as to minimize surface corruption after cleaning. The photoelectron detection will include capabilities for both multichannel, spin-integrated analysis as well as true spin resolved spectroscopy using a MiniMott detection scheme[16].

IV. Acknowledgements
This work was performed under the auspices of the U.S Department of Energy by LLNL (Contract No. W-7405-Eng-48), LANL (Contract No. W-7405- ENG-36) and LBNL (Contract No. DE-AC03-76SF00098). The Spectromicroscopy Facility (Beamline 7.0) and the Advanced Light Source were built and and are supported by the DOE Office of Basic Energy Research. The authors wish to thank Jason Lashley and Michael Blau for synthesis of the Pu samples.

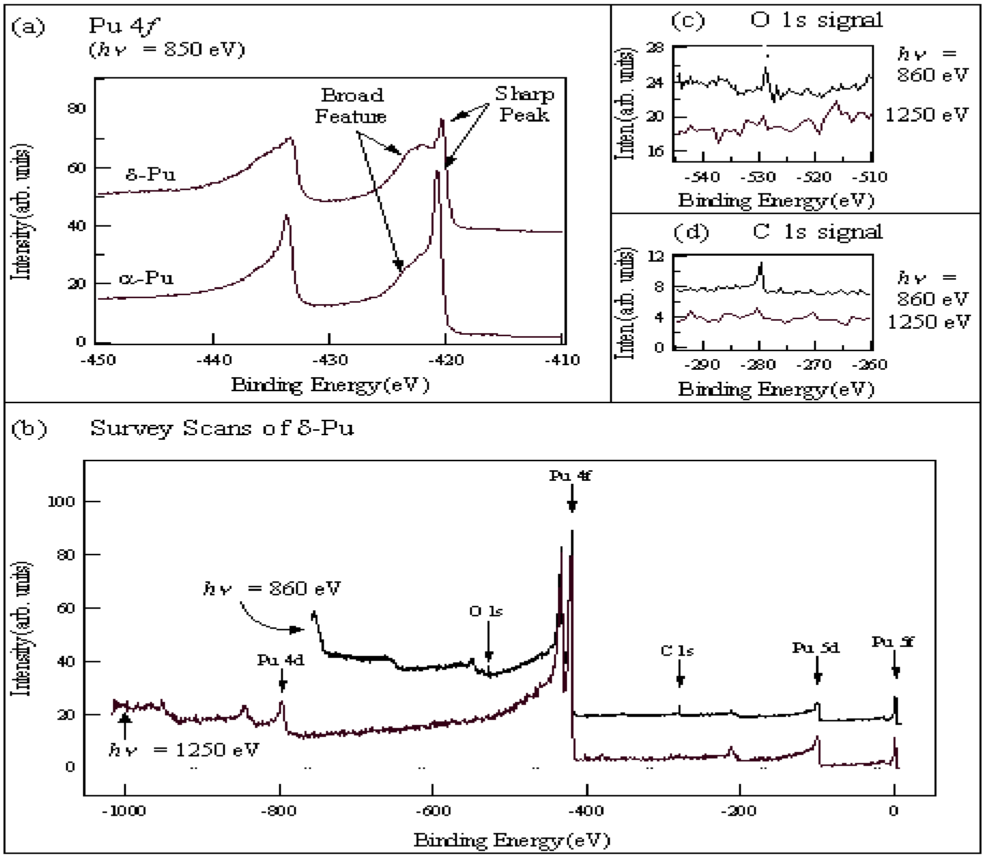

Figure 4 (Left). Core level photoelectron spectroscopy. (a) Detail of the 4f levels of the alpha and delta Pu. (b) Wide scans at both 1250 eV and 860 eV. (c) Detail of the O 1s peak region. (d) Detail of the C 1s peak region.

Figure 5 (Below). Schematic of the new, dedicated Pu Spectrometer.

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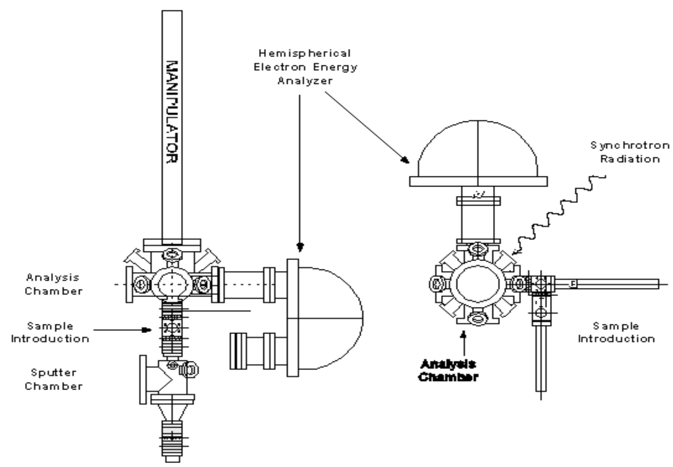

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